DETERMINATION OF ORGANIC ACIDS IN TOBACCO SMOKE BY ION CHROMATOGRAPHY

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SUMMARY

An ion chromatographic procedure was applied to the determination of organic acids in tobacco smoke. Seventeen carboxylic acids were identified positively or tentatively in this study. Formic and acetic acid were the predominant organic acids in the smoke. Examined were the filtration efficiency and the filtration selectivity of the filters of cellulose, cellulose acetate and polypropylene for formic and acetic acid. Cellulose acetate was the highest and polypropylene was the lowest in both filtration efficiency and filtration selectivity for each acid.

INTRODUCTION

The aroma and taste of tobacco are greatly affected by the organic acids in tobacco smoke (1). The composition of the acidic fraction of the smoke has been determined in both quality and quantity by gas chromatography (2-7). The gas chromatographic procedure involved complicated pretreatments such as a simultaneous extraction and methylation or trimethylsilylation. A more convenient and rapid analytical procedure has been desired.

Recently, it was reported that ion chromatography can be used to analyze a wide range of organic acids (8). Baker P.G. and co-wokers have reported using ion chromatography to measure malic, oxalic, and citric acids in tobacco (9).

The research reported here is first a study on the application of ion chromatography to organic acid determination in tobacco smoke, and second a study on filtration of acidic components in the smoke for various filter materials using the ion chromatographic analytical procedure.

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EXPERIMENTAL

Ion Chromatography : The study was performed on a Model IC-500R (Yokokawa-Hokushin Electric Co.) ion chromatograph equipped with a conductivity and a UV detector. Samples were analyzed on a 4 mm ø x 250 mm SCS-5 anion separator column. A 2.0 mM aqueous phosphoric acid solution was used as an eluent at a flow rate of 1.0 ml/min. The column temperature was maintained at 45 °C.

Reagents : All solutions were prepared with deionized water (conductivity > 18 MΩ/cm). All chemicals used were of reagent grade.

Method of Collecting Smoke : Cigarettes available on the market were smoked under standard conditions (1 puff/min, 2 sec/puff, 30 mm in butt length) with a Filtrona constant flow type smoking machine. The smoke was collected in a cold trap cooled with dry ice-methanol.

Extraction of Acids : One hundred ml of deionized water was added into the trap containing the smoke condensate of 10 cigarettes, and the trap was shaken for 30 minutes on a shaker. The aqueous extract was passed through a 0.5 µm membrane filter after shaking.

Identification of Acids : Acids in the smoke were identified by comparing their ion chromatographic retention times with those of authentic compounds.

Calculation of Filtration Efficiency and Selective Filtration Coefficient for Acids :
The filtration efficiency of a filter made of various materials for formic and acetic acids was calculated by the following equation.

$$Ex(\%)=[Wu(x)-Wf(x)]x100/Wu(x)$$

where Ex is the indirect filtration efficiency for component x, Wu(x) is the weight of component x obtained from an "equivalent" nonfilter cigarette, and Wf(x) is the weight of component x obtained from the filter cigarette.

The selective filtration coefficient (Sx) was calculated as follows (10) :

$$Sx=(100-E_{TPM})/(100-Ex)$$

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RESULTS AND DISCUSSION

Identification of Acids : Chromatograms of a typical cigarette smoke sample eluted with the 2.0 mM phosphoric acid are shown in Figure 1, and the substances identified are listed in Table I. About forty substances in the smoke were detected together through conductivity and UV detection, and seventeen carboxylic acids were identified positively or tentatively in this study. Among these substances in the table, ß, ß'-thiodipropionic acid has not been found in preceding articles, so it is necessary to study further using other identification methods in addition to retention time.

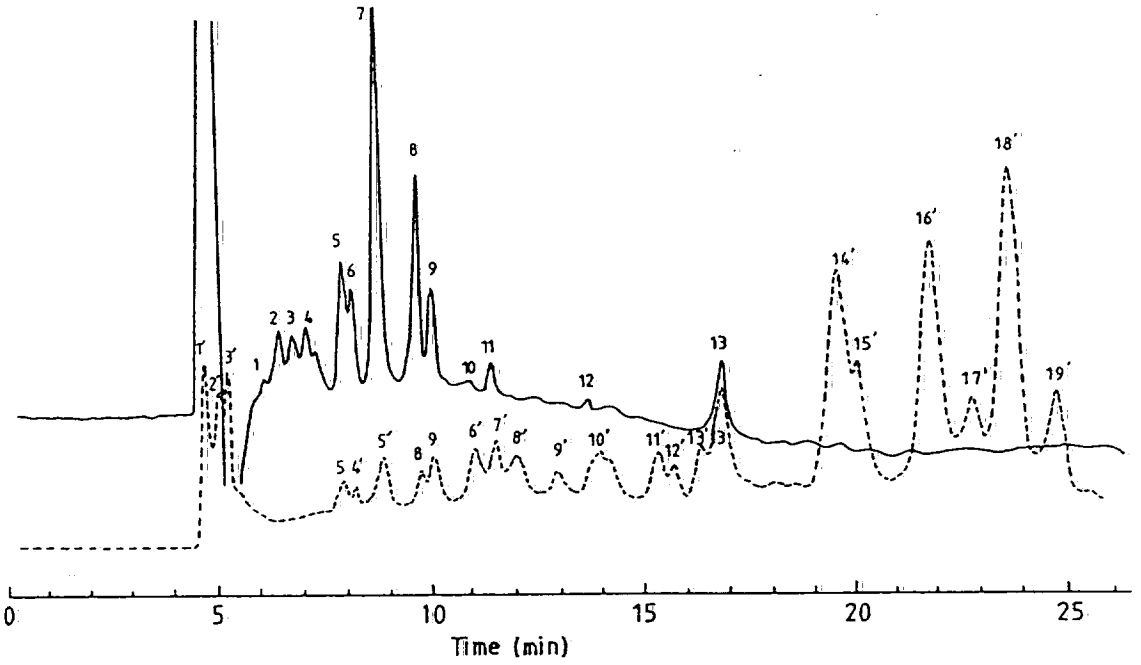

Fig. 1. Ion Chromatogram of Organic Acids in Cigarette Smoke
Detector : Conductivity ———, UV --------

In the longer retention time region, several strong peaks were found using UV detection, though the corresponding ones were scarcely found in conductivity detection. It is considered that the peaks are those of substances in whose molecules the weight ratio of the acid group is low and such structures as unsaturated bonds and /or aromatic rings sensitive to UV are contained. Further investigation is in progress on three peaks 14', 16', and 18' by MS analysis for the fraction collected.

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Formic and acetic acid were the predominant organic acids in the cigarette smoke studied in this paper as noted in the preceding article (7).

Table I Acidic Compounds in Cigarette Smoke (refer to Fig. 1)

Conductivity Detection			UV Detection		
Peak No.	Compounds	Rt. Time (min.)	Peak No.	Compounds	Rt. Time (min.)
1	Succinic acid	6.2	1'	Oxalic acid	4.7
2	Malic acid	6.4	2'	Malonic acid	5.0
3,4	Unknown		3'	Oxalacetic acid	5.2
5	Glycollic acid	7.8	5	Glycollic acid	7.8
6	Itaconic acid	8.1	4',5'	Unknown	
7	Formic Acid	8.6	8'	Acetic acid	9.6
8	Acetic acid	9.6	9	ß,ß'-Dithiopropionic acid	10.0
9	ß,ß'-Dithiopropionic acid	10.0	6'	Unknown	
10	Unknown		7'	Acrylic acid	11.6
11	Propionic acid	11.4	8'	Phthalic acid	12.0
12	n-Butyric acid	13.6	9',10'	Unknown	
13	Pyromucic acid	16.9	11'	Methacrylic acid	15.2
			12',13'	Unknown	
			13	Pyromucic acid	16.9
			14'~19'	Unknown	

Filtration Efficiency and Selectivity : The filtration efficiency of tobacco filter materials for formic and acetic acid was examined for cellulose, cellulose acetate, and polypropylene.

Table II shows the quantitative data of formic and acetic acid delivery for cigarettes with and without filters, as well as the filtration efficiency of each filter for the two kinds of acid and for the dry TPM (total particulate matter). The selective filtration coefficient for the acid was also calculated.

For the filtration efficiency, cellulose acetate was a little bit higher than cellulose, and polypropylene was the lowest. However, all of the fibrous materials examined were

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excellent for filtration selectivity of the acids. Thus cellulose acetate was far superior to the other materials, and polypropylene was judged to be the least effective.

Table II Dependence on Filter Material of Acid Delivery, Filtration Efficiency, and Selective Filtration Coefficient

Filter Material	Non	Cellulose (Neo-filter®)	Cellulose Acetate (f/d:3Y)	Polypropylene (f/d:7Y)
Pressure Drop (mmWG)		48	48	49
Delivery (μg/cig.)				
Formic acid	415	155	137	213
Acetic acid	946	380	366	482
Filtration Efficiency (%)				
Formic acid	–	63	67	49
Acetic acid	–	60	61	49
Dry TPM	–	42	39	36
Selective Filtration Coefficient				
Formic acid	–	1.57	1.85	1.25
Acetic acid	–	1.45	1.56	1.25

Tobacco Column : "Cherry", a commercial product of Japan Tobacco Inc.
Filter : Length 17mm, circumference 24.7mm
Neo-filter ®: Filter made from wood pulp non-woven sheet

Judging from the molecular structure of cellulose acetate it is reasonable to think that cellulose acetate is high in affinity to formic and acetic acid. So, in the case of cellulose acetate filters, the affinity between the cellulose acetate and the acids contributes in large part to the filtration selectivity. In cellulose filters, the high filtration selectivity is considered to be caused by the affinity between the moisture and the acids : cellulose is the highest of the three materials in moisture content.

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